

Electrochemical kinetics

Reaction rates

The **homogeneous reaction rate** (Tllecture 9 p2): $r_{\text{homogeneous}} = \frac{1}{\nu_j} \frac{d[A_j]}{dt}$

There is a more general reaction rate written with mole numbers instead of the molar

concentrations: $r_{\text{general}} = \frac{1}{\nu_j} \frac{dn_j}{dt}$

Relationship: $r_{\text{homogeneous}} = \frac{r_{\text{general}}}{V}$ V is the volume

$r_{\text{homogeneous}}$ is nice for homogeneous reactions, but not usable for heterogeneous ones, like electrode reactions which occur **on the surface** of the electrodes. Here we have to use the **surface concentration** and the **heterogeneous reaction rate**: $r_{\text{heterogeneous}} = \frac{r_{\text{general}}}{A} = \frac{1}{A} \frac{1}{\nu_j} \frac{dn_j}{dt}$

It fits for the electrochemical reactions.

A is the surface

The current density (j) is directly proportional to the heterogeneous reaction rate:

$$j = \frac{I}{A} = \frac{1}{A} \frac{dq}{dt} = \frac{1}{A} \frac{z_j F}{\nu_j} \frac{dn_j}{dt} = z \cdot F \cdot r_{\text{heterogeneous}}$$

Steps of the electrochemical processes

The electrochemical processes are complex heterogeneous ones including several steps:

- transport of the reactant(s) to the surface
- surface reactions including the charge transfer step on phase interface
- adsorption, chemisorption, desorption of the reactants/products, crystal formation

Let us discuss a simple metal electrode with cell reaction: $M^{z+} + ze^{-} \rightleftharpoons M$

The reduction reaction is called cathodic process: $M^{z+} + ze^{-} \rightarrow M$

The oxidation reaction is called anodic process: $M \rightarrow M^{z+} + ze^{-}$

The current densities corresponding to these processes are noted by j_c and j_a .

The net current density: $j = j_c + j_a$

Polarization, equilibrium and polarization potential

If the electrode is left to reach a **steady state** there is no current flowing through the metal, $j=0$.

In this case the electrode potential is called as **steady state potential**. For simple electrodes like this metal electrode it is in equilibrium, so this is **equilibrium potential** (ε_e).

Here $j_a = -j_c$ and the absolute value of them is called **exchange current density of the electrode**: $j_0 = j_a = |j_c|$

If we force some **current flow through the electrode** $j_a \neq -j_c$, therefore its **potential differ from the equilibrium potential** (ε_e). The phenomena is called **polarization**, the potential of the electrode is the **polarization potential**.

The difference of the equilibrium and the polarization potentials is the **overpotential** (η):

$$\eta = \varepsilon - \varepsilon_e$$

If η is positive we have anodic, if negative cathodic polarization.

Polarization curves

One can plot the current density vs. polarization potential (or overpotential), these are called **polarization curves**. Interestingly, they are not linear functions (as we expect from the Ohm's law), but has horizontal sections, „hills” and „valleys”.

The current flowing through the electrode can be limited by various processes.

The two most important ones:

- **charge transfer** (causes charge transfer polarization)
- **diffusion** (causes diffusion polarization)

The polarization curves are quite differently under different limiting processes.

Tafel equation

In 1906 Julius Tafel investigated the hydrogen ion reduction on different metals. He found that the overpotential is proportional to the logarithm of the current density:

$$\eta = a + b \cdot \lg|\tilde{j}|$$

where \tilde{j} is the unitless current density,
a and b are empirical constants.

The Tafel equation was elucidated later by
the Erdey-Grúz – Volmer– Butler equation.

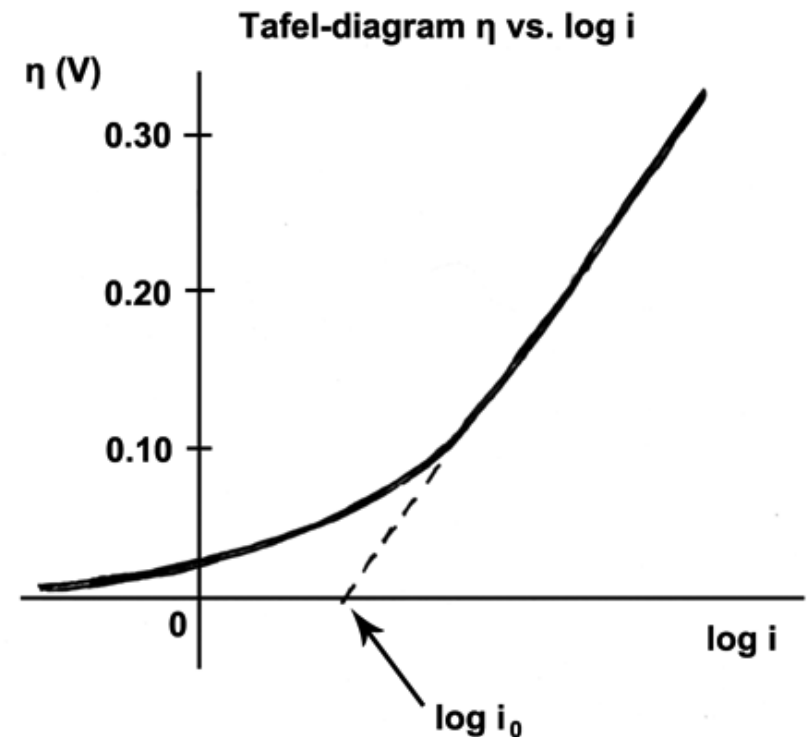


Julius Tafel

Born: 2 June 1862

Died: 2 September 1918

Swiss chemist



Charge transfer polarization

Charge transfer polarization: the limiting step is the charge transfer.

The electric potential of the electrode changes the activation energy of the anodic and cathodic processes, but not with the same amount. Erdey-Grúz, Volmer and Butler investigated the charge transfer coefficient describing this effect.



Erdey-Grúz Tibor

Born: 27 October 1902

Died: 16 August 1976

Hungarian chemist



Max Volmer

Born: 3 May 1885

Died: 3 June 1965

German physical chemist



**John Alfred
Valentine Butler**

Born: 14 February 1889

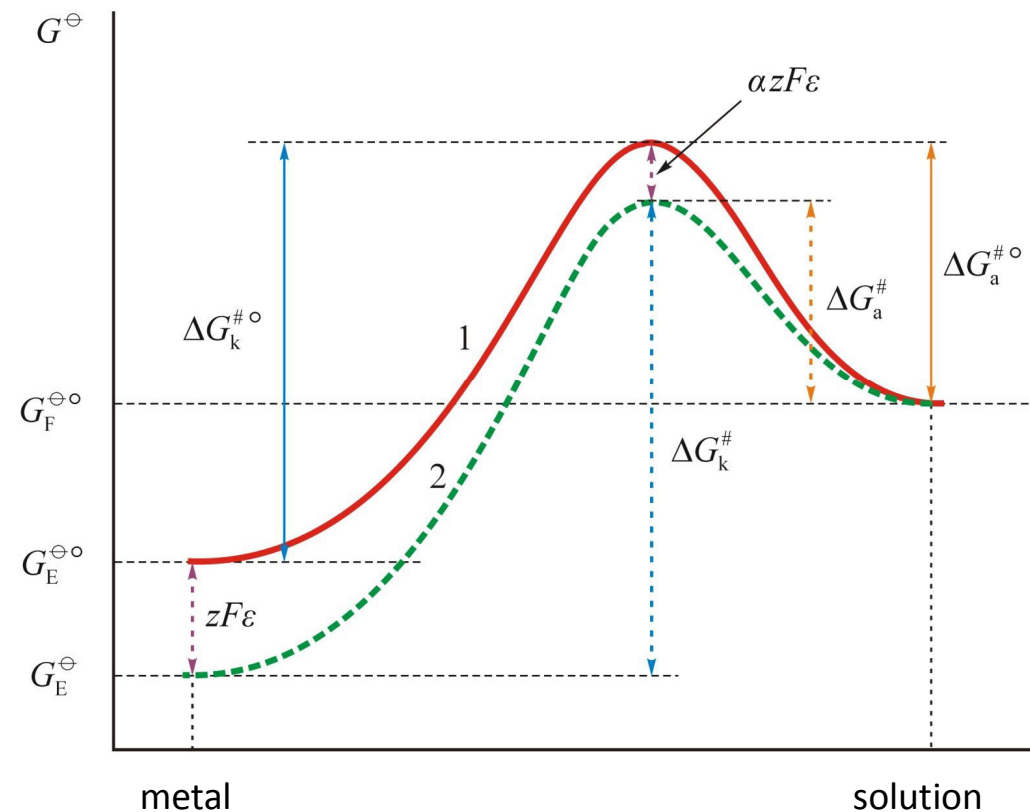
Died: 16 July 1977

English physical chemist

How the potential affects the activation Gibbs free energies?

If the potential of the electrode metal changes the activation energy of both reaction changes, but with different quantity.

One way by $\alpha zF\varepsilon$, the other by $(1 - \alpha)zF\varepsilon$ where α is the charge transfer coefficient.



The Erdey-Grúz – Volmer – Butler equation

The anodic and cathodic current densities depend on the overpotential exponentially:

$$j_a = j_0 \exp \left[\frac{\alpha z F \eta}{RT} \right]$$

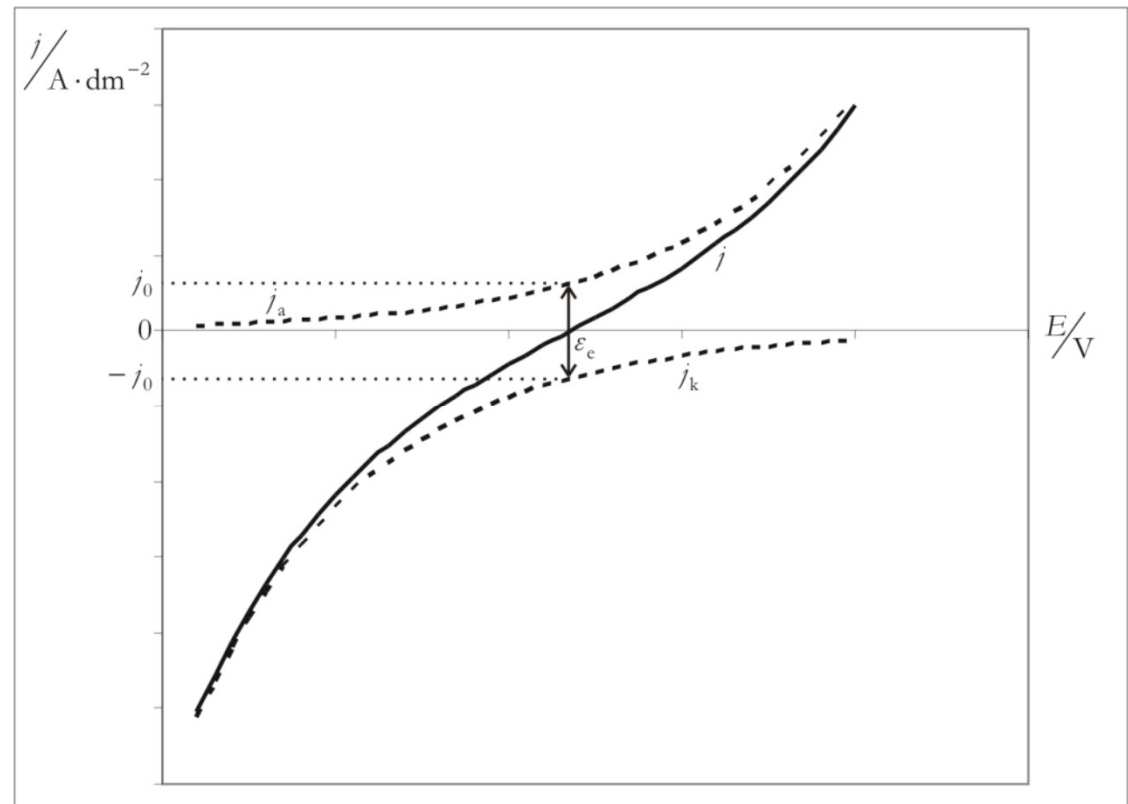
$$j_c = -j_0 \exp \left[-\frac{(1-\alpha) z F \eta}{RT} \right]$$

According this the net current density:

$$j = j_0 \left(\exp \left[\frac{\alpha z F \eta}{RT} \right] - \exp \left[-\frac{(1-\alpha) z F \eta}{RT} \right] \right)$$

This equation is called as

Erdey-Grúz – Volmer – Butler equation.



Typical polarization curve
for charge transfer polarization.

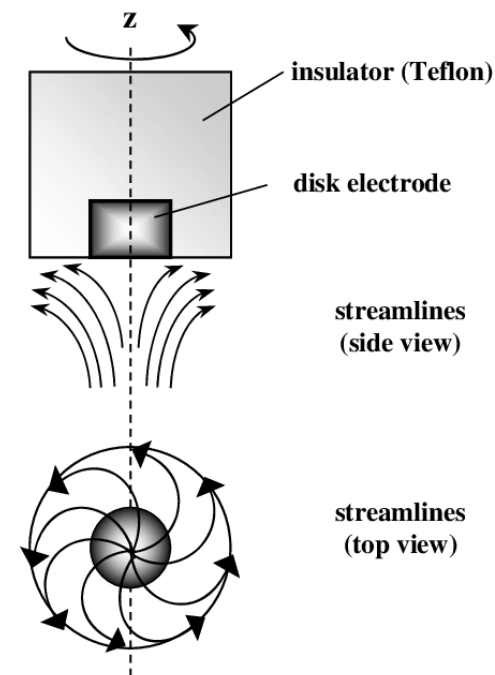
Diffusion polarization

Diffusion polarization: the limiting step is the diffusion.

Based on the Fick's laws we can describe the charge transport phenomena. Increasing the current density the surface concentration of the reactants decreases because the transport can not carry enough species to the surface.

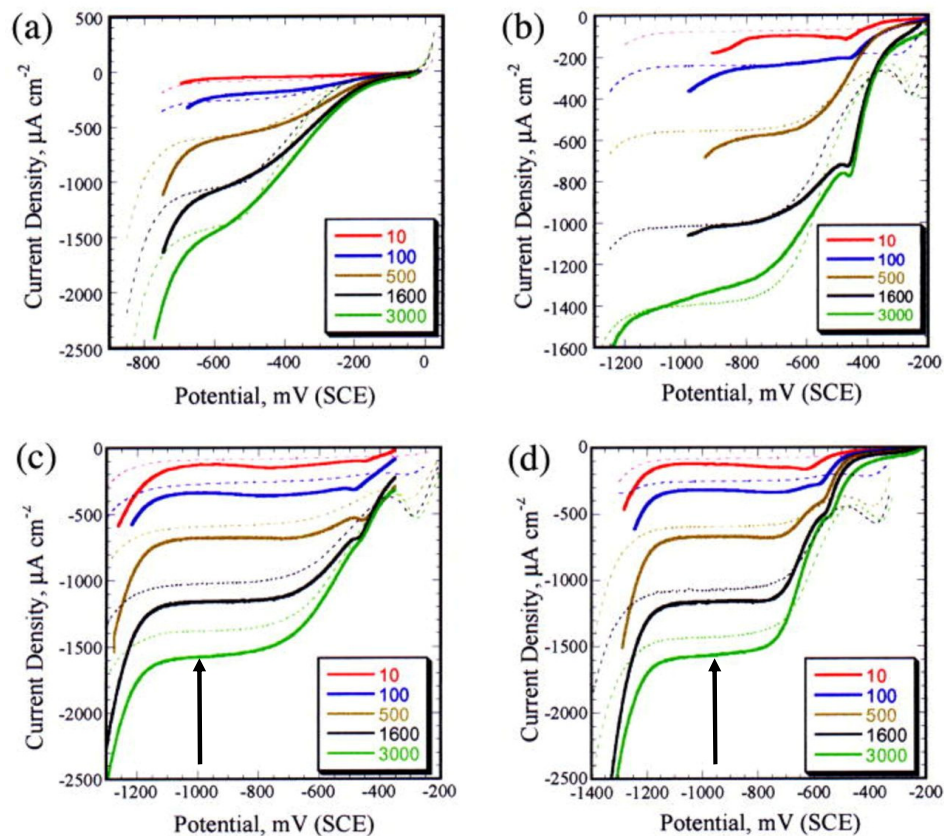
At a limiting current density **the surface concentration becomes zero** and the current density can not be larger than this value, the **diffusion limited current density**.

The diffusion limited current (density) depends on the width of the diffusion layer which can be adjusted using a **rotating disk electrode**.



Streamlines of the rotating disc electrode.

Polarization curves on polycrystalline Cu disks at prescribed disk rotation rates obtained in 0.1 M Na₂SO₄ at pH x .



M. B. Vukmirovic et al. J. Electrochem. Soc. 2003;150:B10-B15

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The current density of species i is proportional to the square root of the angular frequency described by the Levich equation:

$$j_i = -0.62 \frac{z}{\nu_i} F D_i^{2/3} \nu^{-1/6} \omega^{1/2} c_i$$

ν_i is the stoichiometric coefficient of species i

D_i is the diffusion coefficient of species i

ν is the kinematic viscosity of the solution

ω is the angular frequency

c_i is the bulk concentration of species i



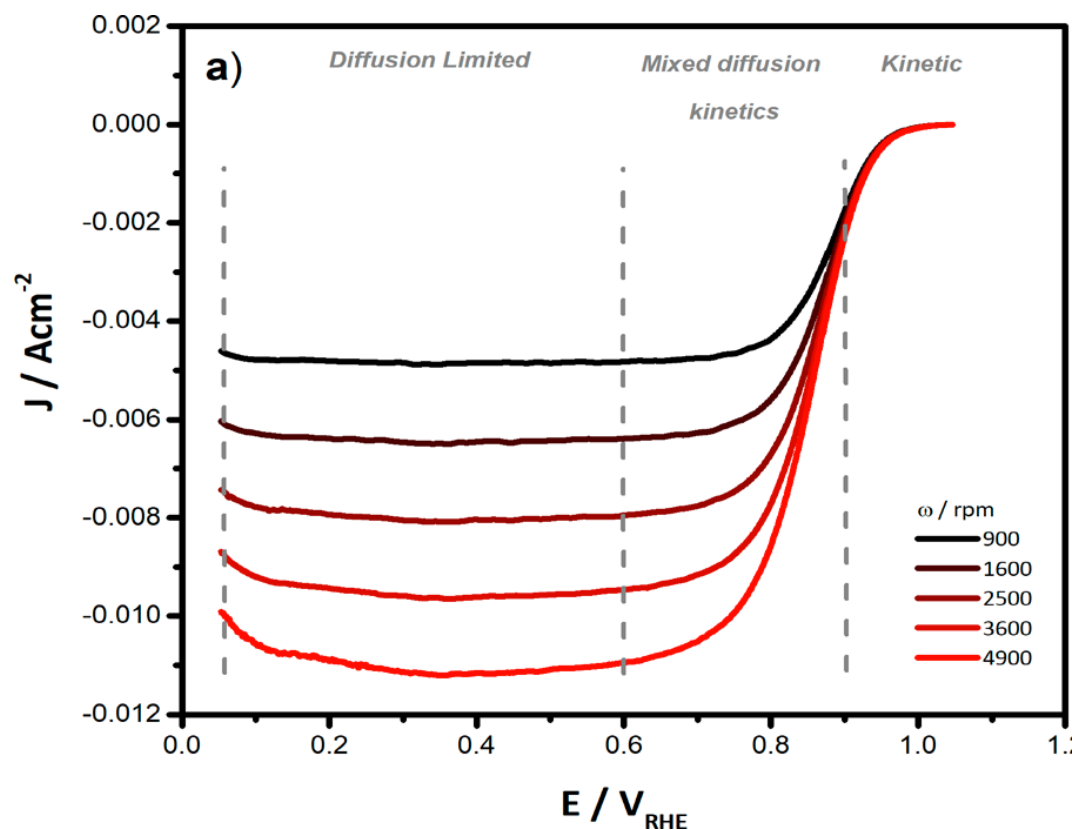
Вениамин Григорьевич Левич
(Veniamin Grigorievich Levich)

Born: 30 March 1917

Died: 19 January 1987

Physical chemist

Diffusion or charge transfer polarization?



ACS Appl. Mater. Interfaces 2017, 9, 44, 38176-38180
DOI: 10.1021/acsami.7b13902, Figure 1 (a)